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A small team comprising of scientists from France, the United Kingdom, Japan and the U.S., has performed collaborative research on high T_c ceramic superconductors and inorganic nonlinear optical composites, the $BiCuSrCaO_x$ system was found to be glass-forming. The glass can be crystallized to give a superconducting glass-ceramic was machinable. The glass was also infrared transmitting to about 7 microns. nanocomposites containing crystallites of CdS in both glass and organically-modified silicates (ORMOSIL) have been prepared via the sol-gel technique. Quantum confinement was demonstrated in these nonlinear optical materials.

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Submitted by

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ABSTRACT

A small team comprising of scientists from France, the United Kingdom, Japan and the U.S., has performed collaborative research on high T_c ceramic superconductors and inorganic nonlinear optical composites. the $BiCuSrCaO_x$ system was found to be glass-forming. The glass can be crystallized to give a superconducting glass-ceramic was machinable. The glass was also infrared transmitting to about 7 microns. Nanocomposites containing crystallites of CdS in both glass and organically-modified silicates (ORMOSIL) have been prepared via the sol-gel technique. Quantum confinement was demonstrated in these nonlinear optical materials.

1. INTRODUCTION AND BACKGROUND

Future advances in engineering systems are primarily governed by innovative designs and the availability of improved and/or new engineering materials. In a general sense, an engineering system can include large objects such as a space-craft and a space-platform or a small component of a large system such as an infrared sensor device. The continuing research on how structure, microstructure and chemical composition can influence the properties of existing materials is of obvious importance if the properties of materials are to be extended or if new materials are to be made. Frequently, more than one route is available for the synthesis of solids. For instance, a material may be prepared by vapor phase reactions, liquid state reactions, or solid state reactions. When a material has been synthesized, it must be fabricated into some shape prior to its utilization in a device. Again, more than one route may be available for fabrication. For example, a metallic objective of some special shape may be fabricated via solid state forming, liquid state casting or vapor phase deposition. The resultant properties of the end object are often influenced by the method of fabrication.

Recently, chemical processing has become increasingly important for the synthesis of electronic and structural materials.[1] For example, the metal-organic polymer route has been extensively investigated for the synthesis of structural ceramics such as silicon carbide and silicon nitride.[2] The sol-gel route has separately been widely studied for the preparation of oxides.[3] In addition, both methods are highly versatile in that they can be used to fabricate materials as well. Thus, the metallic-organic polymer method has been used to fabricate SiC fibers [4] The sol-gel technique has been successfully applied for

the fabrication of thin films, fibers and monoliths.[5] With these successes also came the realization that the sol-gel process can only be successfully exploited if a multidisciplinary effort is assembled. This is because of the complexity of the process and the current lack of sufficient knowledge.

In 1987, Dr. D.R. Ulrich of the AFOSR and SDIO, recognizing the need to assemble the most qualified team of scientists to make rapid advances in the development of the new superconducting ceramics, conceived the idea of an international collaborative research program to exploit the joint expertise of both U.S. and foreign scientists. In September, 1987, the present grant (F-499620-87-K-0011) was awarded to UCLA with Professor J.D. Mackenzie as principal investigator. He would investigate the fabrication of ceramic superconductors from the liquid route, especially the sol-gel route. Professor J. Livage of the University of Paris, France, was selected as a collaborator to study the chemistry of liquid solutions which were sol-gel precursors. Professor A. Wright of the University of Reading, Untied Kingdom, was selected as a third member of the team to perform structural analysis of sol-gel related solids by X-ray and neutron diffraction.

In 1988, the UCLA group discovered the glass-forming tendency of superconducting ceramics based on the Bi-Sr-Ca-Cu-O system. Since the glass would crystallize under controlled heat-treatment to give dense polycrystalline superconductors, it became logical to include this aspect of processing to the on-going program.

In 1989, at the suggestion of Dr. Ulrich, a new effort was launched through the augmentation of the original grant to permit J.D. Mackenzie to initiate a small research project on nonlinear optical nanocomposites in collaboration with Professor M. Yamane of the Tokyo Institute of Technology, Japan. This was because oxide glasses containing microcrystals of CdS_xSe_{1-x}

have received a great deal of attention as new non-linear optical materials for applications in nonlinear signal processing and optical devices.[6] Because the glass was made via high temperature melting, the control of the size of the semiconductor crystallites was difficult.[7] The sol-gel process conceivably could be a superior method to prepare these new nonlinear materials. Thus, the present program was expanded to incorporate the sol-gel processing of these nanocomposites.

These program has resulted in some very fruitful collaborations between UCLA, the University of Paris, Reading University of Britain and the Tokyo Institute of Technology. Research progress made between October 1, 1987 and September 30, 1990 is summarized in this Final Technical Report.

II. INTERNATIONAL COLLABORATION

The total research effort under the present grant has been a relatively small one. At UCLA, the team basically consisted of Professor J.D. Mackenzie, one postdoctoral scholar and one graduate student performing research on high Tc ceramic superconductors. Subcontracts were made to the University of Paris and to Reading University, U.K. by UCLA to support one graduate student under Professor J. Livage and one graduate student under Professor A. Wright. For the more recently established project on nonlinear optical nanocomposites, an additional graduate student was funded at UCLA. Professor M. Yamane shared the supervision of this student with professor Mackenzie. Professor Yamane's travel expenses between Tokyo and Los Angeles and his stay at UCLA for three weeks were funded through this grant.

A. Research Performed by Professor J. Livage in France

Professor Livage's research has been concerned with the solution chemistry of precursors for superconducting oxides. One technique his group had been investigating was the coprecipitation of oxalates. The 1:2:3 superconductors prepared by this was found to have very low critical current density. A second method was then explored via the use of mixed organic and inorganic networks during solution polymerization. The superconductors produced were found to contain carbon. A new method using hydroxides was developed which should obviate the carbon problem.

B. Research Performed by Professor A. Wright in the United Kingdom

Professor A. Wright has been studying the amorphous phases of the 1:2:3 gels and the glassy phases of the bismuth system via X-ray diffraction and neutron scattering. Samples of these disordered solids were supplied by the UCLA group. Neutron scattering experiments have been performed at the Harwell Laboratory and the Rutherford Appleton Laboratory in Oxfordshire, U.K. The samples have been studied as a function of heat-treatment time and temperature in order to correlate the structures of the amorphous and crystalline phases. Preliminary results indicated that this type of investigations could lead to a better understanding of the complex transformations of the amorphous phases into the various crystalline phases. Some of the data obtained are now being analyzed.

C. Interactions between the Four Groups

a. Professor J.D. Mackenzie visited Professor Wright at Reading University

for one day in the summer of 1988 and for five days in the spring of 1989. A return visit was paid by Professor Wright to UCLA for two days in 1989.

b. Professor J. Livage visited UCLA in December, 1989 and spent two days with Professor Mackenzie and his assistants.

c. Professor M. Yamane spent two weeks at UCLA in the fall of 1989 and one week in the Spring of 1990 to work on the CdS-oxide glass project.

d. Professors Mackenzie and Livage met at the First OGAMM Symposium in Pitlocry, Scotland in the summer of 1988.

e. Professors Mackenzie, Livage and Wright met at the Second OGAMM Symposium in Ilkley, England in the summer of 1989.

f. Samples of CdS/glass composites made by Professor Yamane have been made available to Professor Mackenzie for evaluations.

III. RESEARCH ON T_c SUPERCONDUCTORS

The sol-gel method is well-known for its many distinct advantages. These include ultrahomogeneity of the gel and the ability of the starting liquid solutions to become highly viscous. The high viscosity is necessary for the fabrication of fibers and tapes. For the Y-Ba-Cu-O ceramics (1:2:3), alkoxides of Y, Ba and Cu are needed for gel preparation. However, at the beginning of this program, alkoxides of Y and Cu were not available from vendors. Techniques were therefore developed for the synthesis of these alkoxides. After the successful preparation of these alkoxides, it was found that (a) the three alkoxides were not miscible in solutions and (b) the solubilities of individual alkoxides were very low in alcohols. An innovative technique was then developed to obtain a homogeneous solution containing all three alkoxides. A

second technique was developed to prevent precipitation when the solvent was being removed to obtain a viscous solution.

Thin films, fibers and bulk samples were fabricated with these solutions and converted to polycrystalline superconductors of the 1:2:3 composition. A patent disclosure was made to the University of California patent office. Results of the research were presented at various meetings and published (see publications and presentations lists) separately, the chemical solutions were made more viscous by the addition of chelating agents. Fibers were also drawn from these new solutions. The synthesis of a homogeneous solution containing Y and Cu is shown in Fig. 1 as well as the preparation of the 1:2:3 superconductor. Ceramic fibers made by hand are shown in Fig. 2. The AC susceptibility of a superconducting ceramic powder obtained from grinding of the fibers shown in Fig. 3. The conductivity of a 1:2:3 film formed on a single crystal MgO substrate is shown in Fig. 4. Perhaps the most interesting feature of the thin film is the preferred orientation as grown on the MgO substrate (Fig. 5). This suggests the possibility of the growth of single crystal film if the structure of the sol-gel solution can be better controlled.

B. Superconducting Ceramics by the Glass-to-Ceramic Route

Although it is relatively easy to prepare the 1:2:3 and the $BiCaSrO_x$ superconductors by the sol-gel method, the polycrystalline ceramic obtained is usually very porous. The elimination of pores requires long periods of heating at elevated temperatures. In 1988, we discovered that the bismuth composition was glass-forming and that the glass could be crystallized to give a superconducting glass-ceramic of very low porosity.[8] Thus, not only was the need to densify for long times obviated, but an added advantage was the ease

of fabrication of the glass into various shapes. Samples cast in the form of a rod and a ring are shown in Fig. 6. Typical properties of the glass and glass-ceramics are shown in Table 1. The glass-forming region of this system was rapidly explored and presented in Fig. 7. Examples of a glass fiber drawn by hand and the superconducting ceramic fiber are shown in Fig. 8. When a glass-ceramic rod was fractured, the crystallites were found to exhibit preferred orientation such that the long direction of the rod was along the conductive directions of the crystal (a and b axis) [Fig. 9]. The mechanical properties of the glass-ceramic were comparable to those of common glasses and ceramics as given in Table 2.

Various oxides such as PbO were added to the original bismuth composition and did not appear to influence the electrical property of the glass-ceramic appreciably with the exception of Ga_2O_3. No superconductor was prepared in the latter case. The addition of PbO was particularly attractive since the viscosity of the melt was increased which made fabrication into fibers and tapes easier. The electrical conductivity of the PbO-containing sample is shown in Fig. 10. Another interesting feature of the glass-ceramic was its machinability presumably because of the layered structure of the crystal. A sample of the machined glass-ceramic is shown in Fig. 11.

Up to the present, the measured critical-current density, J_c, of all the glass-ceramic samples was less than 1000 Amps/cm^2. The cause of this low J_c values is not understood. One possibility is the presence of non-conducting phases at the grain boundaries. It was also found that the crystallization process of the glass was highly complex such that the highest T_c phase (2223, T_c = 110°K) could only be obtained via the lower T_c phase (2122, T_c = 80°K). Further, the transformation process is critically dependent on the availability of oxygen in the ambient atmosphere and the diffusion of the oxygen into the

sample. The transformation mechanism and kinetics are now being investigated.

C. IR Transmission of the Bismuth-Containing Glasses

Despite the high concentrations of Ca, Sr and Cu ions, glasses of the bismuth system were found to be relatively transparent in the infrared. The transmission was comparable to that of the fluorozirconate glasses as shown in Fig. 12. These bismuth glasses are however much more chemically durable than the fluorozirconates and have higher glass-transition temperatures. Structural studies are now in progress.

IV. RESEARCH ON NONLINEAR OPTICAL NANOCOMPOSITES

Semiconductors like CdS and CdSe are known to have very high values of third order nonlinear coefficients ($\chi^{(3)}$) at T < 20°K. The very low temperatures needed are not attractive for applications. Theoretically, if the crystal size is reduced to much less than 100Å, of the order of the dimensions of a phonon, quantum confinement occurs. Very high $\chi^{(3)}$ now achievable at room temperatures. Commercial colored glasses containing CdS and CdSe, long used as red and yellow filters, were found to have CdS and CdSe crystallites of about 100Å. Their $\chi^{(3)}$ values were found to be 10^{-8} - 10^{-10} esu at 20°C. Because these glass filters are made by glass fusion methods at high temperatures, and because the mechanisms of crystallite formation are not understood and hence control is difficult, other methods to prepare such *semiconductor quantum dot materials* have become desirable research projects. This program involves the preparation of such nanocomposites by the

sol -gel method. Cuprous chloride microcrystals have also been studied since they also give high $\chi^{(3)}$.

The sol-gel process to prepare semiconductor-doped glasses is superior to the conventional melt-quench method, since the size and the amount of semiconductor dopant can be controlled easily. The sol-gel method can also give glasses with new compositions, high purity and good homogeneity at temperatures significantly lower than those required by the melting method. The semiconductor microcrystallites formed in the melting method are created by complex crystal growth during heat treatment, while those formed via the sol-gel process are by chemical reactions at low temperature. For all optical elements, low temperatures are preferable to high temperatures.

A. Fabrication of Semiconductor-Oxide Nanocomposites by the Sol-Gel Process

Various methods of obtaining semiconductor-oxide nanocomposites have been studied. Two different matrix systems were investigated to prepare these nanocomposites. In the first multicomponent silicate glass system, the sols containing Cd^{2+} were prepared by adding aqueous solution of Cd salt and sodium acetate to the methanol solutions of partially hydrolyzed mixture of tetramethylorthosilicate and boron ethoxide. Gelation of the sols were accomplished by ultrasonic agitation. The obtained gels were heat-treated at around 430°C to decompose the remaining organics and, subsequently, expose to H_2S stream to sulfidize CdO in the heat-treated gel. The CdS-doped porous glasses were fully densified at a temperature as low as 550°C.

The second type of matrix used was organically modified silica (Ormosils). Part of the bridging oxygen bonds in ormosils were replaced by alkyl groups by adding 10 wt.% of polydimethylsiloxane into a

tetraethylorthosilicate alcohol solution. The resulting ormosils were highly transparent. The organic groups present decrease the risk of fracture on drying. Both cadmium sulfide and cuprous chloride have been doped in these ormosils. Cadmium sulfide can be formed by the same method as mentioned above. In the later case,CdS microcrystallites were formed by the reaction of Cd salts and sulfur containing compounds, such as thiourea and thioacetamide. By utilizing colloidal technology, the semiconducting microcrystallites can be formed in the solids prior to gellation. Cuprous chloride were formed in the ormosils by heat treatment. During the heat treatment, nucleation and growth of semiconducting microcrystallites occurred as a result of a diffusive phase decomposition of the supersaturated solid solution. Figure 13 shows the CdS and CuCl semiconductor-oxide nanocomposites prepared by the methods described above.

B. Structural Characterization of the Semiconductor-Oxide Nanocomposites

Formation of semiconducting microcrystallites was observed by a color change of the composites. Exposing the CdO-doped ormosils to H_2S gas changed the transparent sample from colorless to yellow. The coloration was dependent on both the heat treatment and the time of exposure.

Figure 14 shows the X-ray (XRFD) pattern of ormosils heated to 380°C for 24 h (a), reacted with H_2S gas for 8 h (b) and 72 h (c) at room temperature. The ormosils heated at 380°C for 24 h only shows the typical amorphous pattern, whereas the XRD patterns of ormosils reacted with H_2S gas have several broad peaks on the amorphous background of matrices. The precipitated crystallites are identified as hexagonal wurtzite CdS crystals. The particle sizes estimated by the Scherrer equation are 35Å for sample (b) and 60Å for sample (c).

Transmission electron micrograph and electron diffraction pattern of fracture surface are shown in Fig. 15. Both Fig. 15 and Fig. 14 are from the same sample. Cadmium sulfide clusters show faint images in the micrograph with the same average size as estimated by XRD pattern. Selected area diffraction pattern (SAD) shows these clusters having a hexagonal wurtzite structure.

C. Optical Spectra

Figure 16 shows the transmission spectra of ormosils heated for 24 h at 380°C (a), exposed to H_2S gas for 8 h (b) and 72 h (c) at room temperature. It is apparent that the absorption edge of (b) is blue shifted by 0.25eV compared to (c). The blue shift is attributed to the quantum size effect of the carrier confinement.

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25. Choi, Y.S., Zheng, Haixing and Mackenzie, J.D., "Preferred Orientation of Bi-Ca-Sr-Cu-O Superconductors via Glass-Ceramic Route," to be submitted to J. of American Ceramics Society.

Invited Presentations

1. Mackenzie, J.D., "Fabrication of High Tc Superconductors from Solution and Glass Ceramic Routes."

2. Zheng, Haixing and Mackenzie, J.D., "Preparation and properties of Bismuth-Based Ceramic Superconductors from Glasses."

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Presentations

1. Zheng, Haixing, Sanghera, J.S., and Mackenzie, J.D., "GlassFormation and Properties of the Quaterary AlF_3-BaF_2-CaF_2-ZrF_4 System," 1989 Glass Meeting, American Ceramic Society, September, 1989, Lake Buena Vista, Florida.

2. Zheng, Haixing, Chen, K.C., and Mackenzie, J.D., "Superconducting $YBa_2Cu_3O_{7-x}$ Fibers Prepared by the Sol-Gel Process," Materials Research Society Spring Meeting, April, 1988, Reno, Nevada.

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13. Xu, Ren, Zheng, Haixing and Mackenzie, J.D., "Preferentially Orientated Crystallites of $Bi_2CaSr_2Cu_2O_x$ Ceramics Formed during Phase Transformation," First intl Ceramic Science and Technology Congress, October, 1989, Anaheim, CA.

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20. Zheng, Haixing, Lin, Patrick and Mackenzie, J.D., "Properties of the IR Transmitting Bi-Ca-Sr-(Cu,Zn)-O Glasses Dop[ed with Lead Oxide," SPIE's 1990 Annual Meeting, July, 1990, San Diego, CA.

Patents

1. Zheng, Haixing, Chen, K.C., Pope, E.J.A., Uchikawa, F., and Mackenzie, J.D., "Solution Process for Making Superconducting Ceramic Articles," patent pending.

2. Zheng, Haixing and Mackenzie, J.D., "Fabrication of Bi-Ca-Sr-Cu-O High T_c Superconductors by the Glass Ceramic Process," patent pending.

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Table 1

Properties of $Bi_4Ca_3Sr_3Cu_4O_{16}$ Glass and Glass Ceramics

$Bi_4Ca_3Sr_3Cu_4O_{16}$ Composition		
	mole%	wt%
Bi_2O_3	16.7	54.0
CaO	25.0	18.0
SrO	25.0	18.3
CuO	33.3	18.3

$Bi_4Ca_3Sr_3Cu_4O_{16}$ Glass	
Glass transition temperature, T_G (^oC)	410
Crystallization temperature, T_X (^oC)	458
Density (g/cm^3)	5.77
Infrared cutoff (μm)	5.5
Thermal expansion coefficient ($10^{-5}/^oC$)	1.326
Electrical resistivity (Ω-cm)	10^7

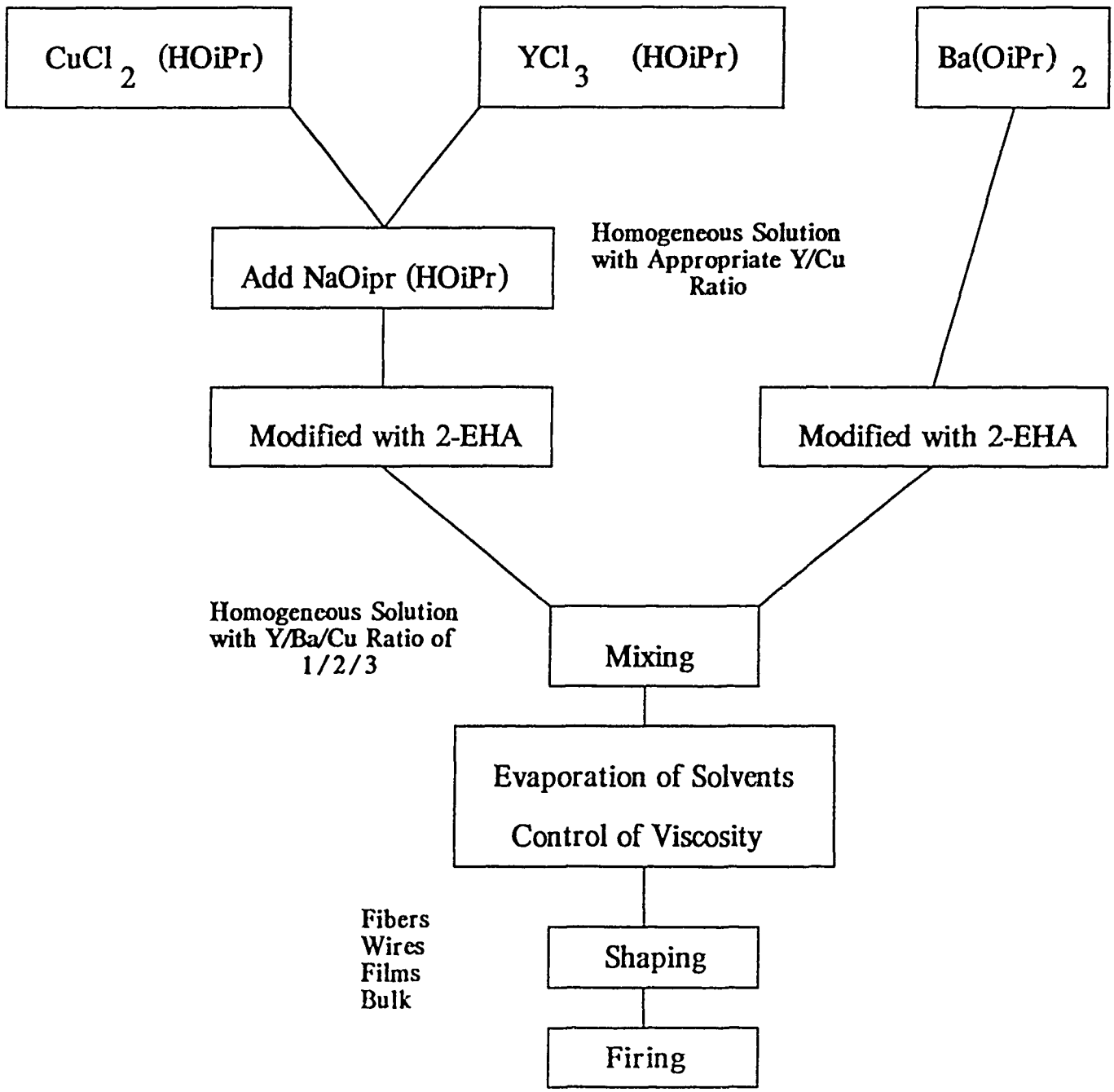
$Bi_4Ca_3Sr_3Cu_4O_{16}$ Glass Ceramics	
Density (g/cm^3)	6.25
Compressive strength (psi)	2×10^4
The Vicker's hardness (kg/cm^2)	600
Superconducting transition temperature (^oK)	
onset	~100
zero-resistance	73

Table 2

Mechanical Properties of Bi-Ca-Cu-O Glass and Superconducting Glass-Ceramic Compared with Some Other Materials

Material	Hardness (GPa)	Young's Modulus (GPa)	Fracture Toughness (MPa/$\overline{m}$)	Strength (Mpa)
Bi-Ca-Sr-Cu-O Glass	~4.5	------	~1.4	~80
Bi-Ca-Sr-Cu-O Glass-Ceramic	~6.0	~90	~2.0	~60
Soda-lime Glass	~5.5	~70	~0.74	~70
Pyroceram Glass Ceramic	~8.0	~108	~2.5	~190
"Soft" Steel	~1.62	~200	~170	~280
Lead Alkali Glass	~4.9	~65	~0.68	----

Figure 1 Synthesis of Modified 1:2:3 Alkoxide Solutions and Processing of 1:2:3 Fibers.



HOiPr: isopropanol

2-EHA: 2-ethylhexanoic acid

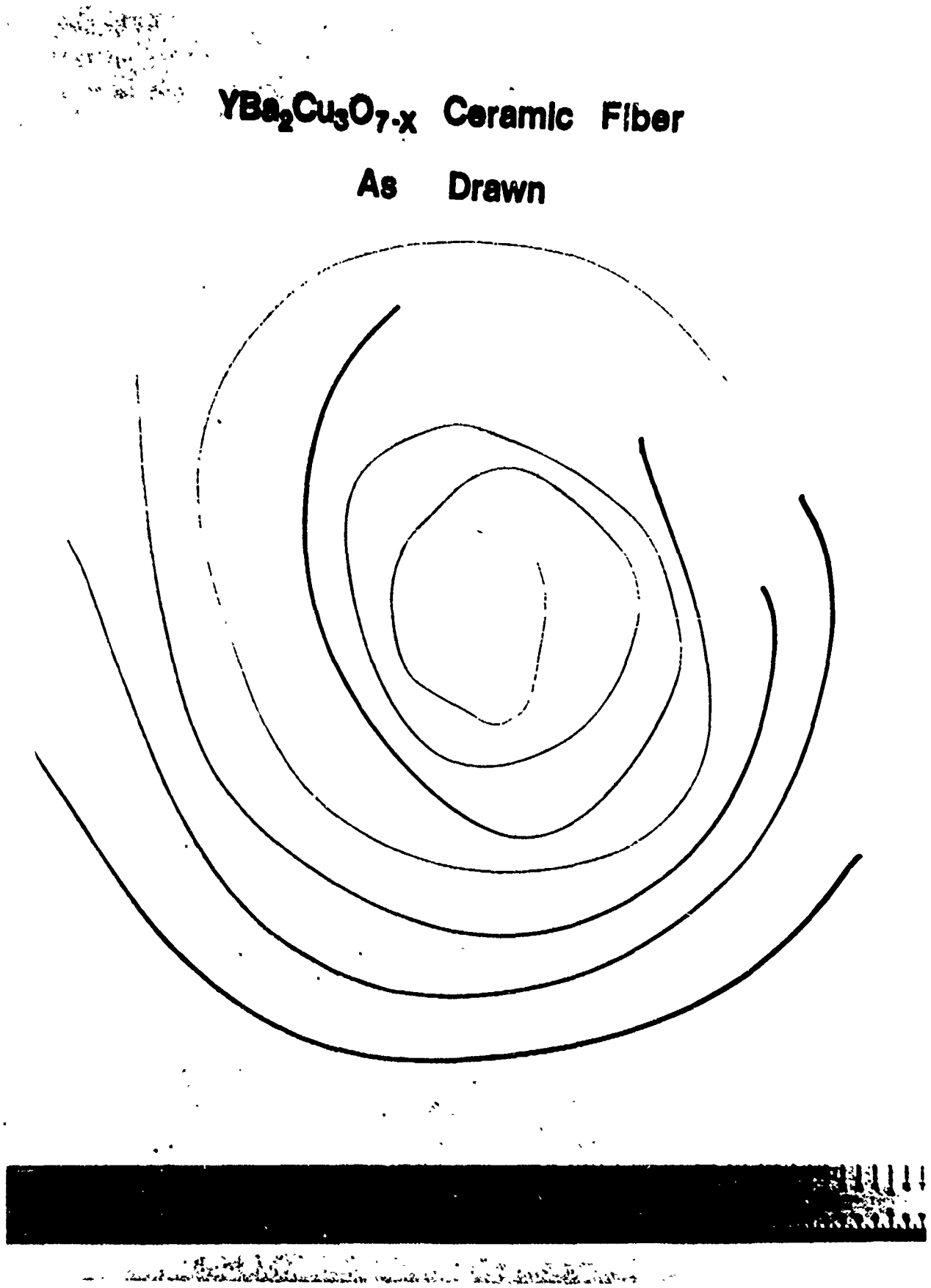


Figure 2. Y-Ba_2-Cu_3-O_{7-x} Ceramic Fiber

Figure 3

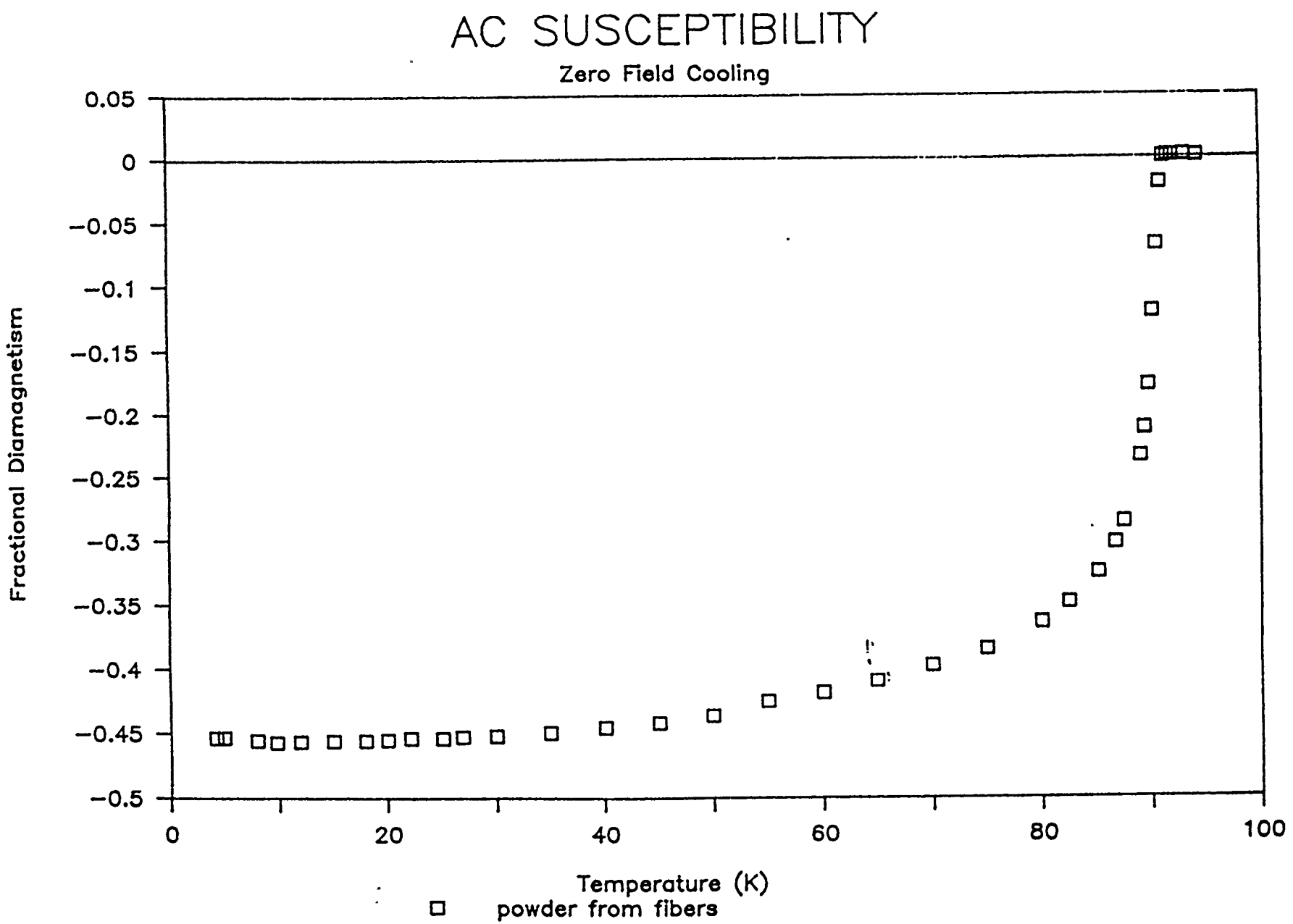
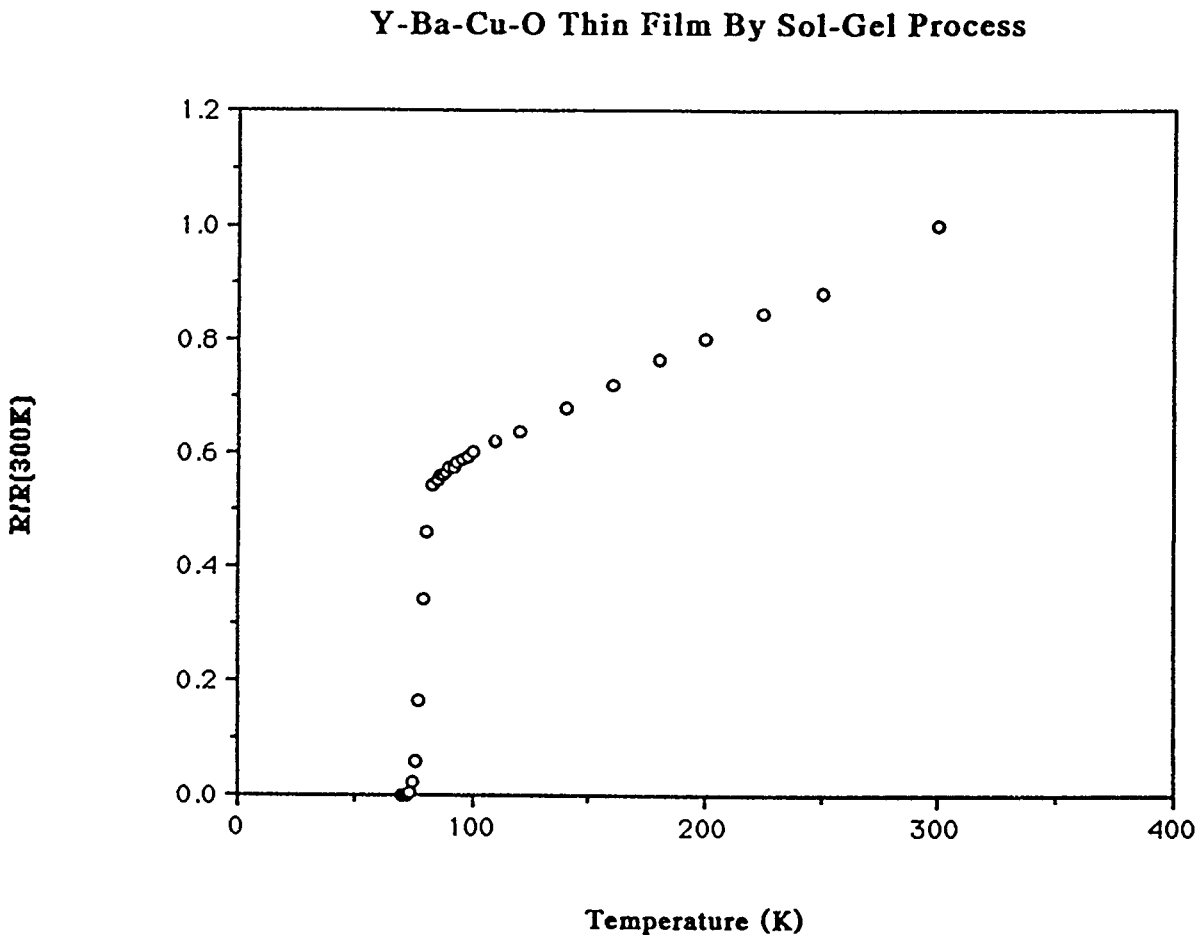

AC SUSCEPTIBILITY
Zero Field Cooling
Fractional Diamagnetism
0.05
0
−0.05
−0.1
−0.15
−0.2
−0.25
−0.3
−0.35
−0.4
−0.45
−0.5
0
20
40
60
80
100
Temperature (K)
powder from fibers

Figure 4


Y-Ba-Cu-O Thin Film By Sol-Gel Process
R/R(300K)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
Temperature (K)

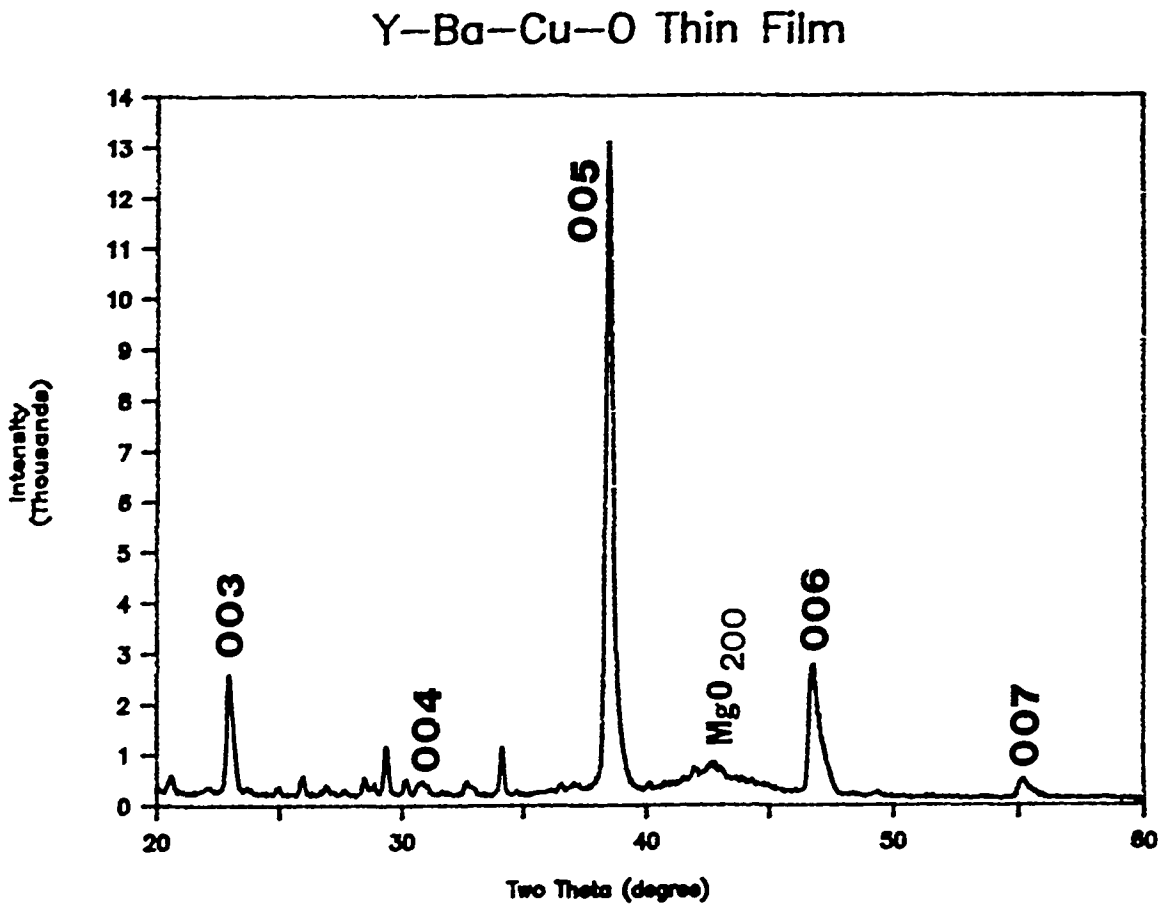
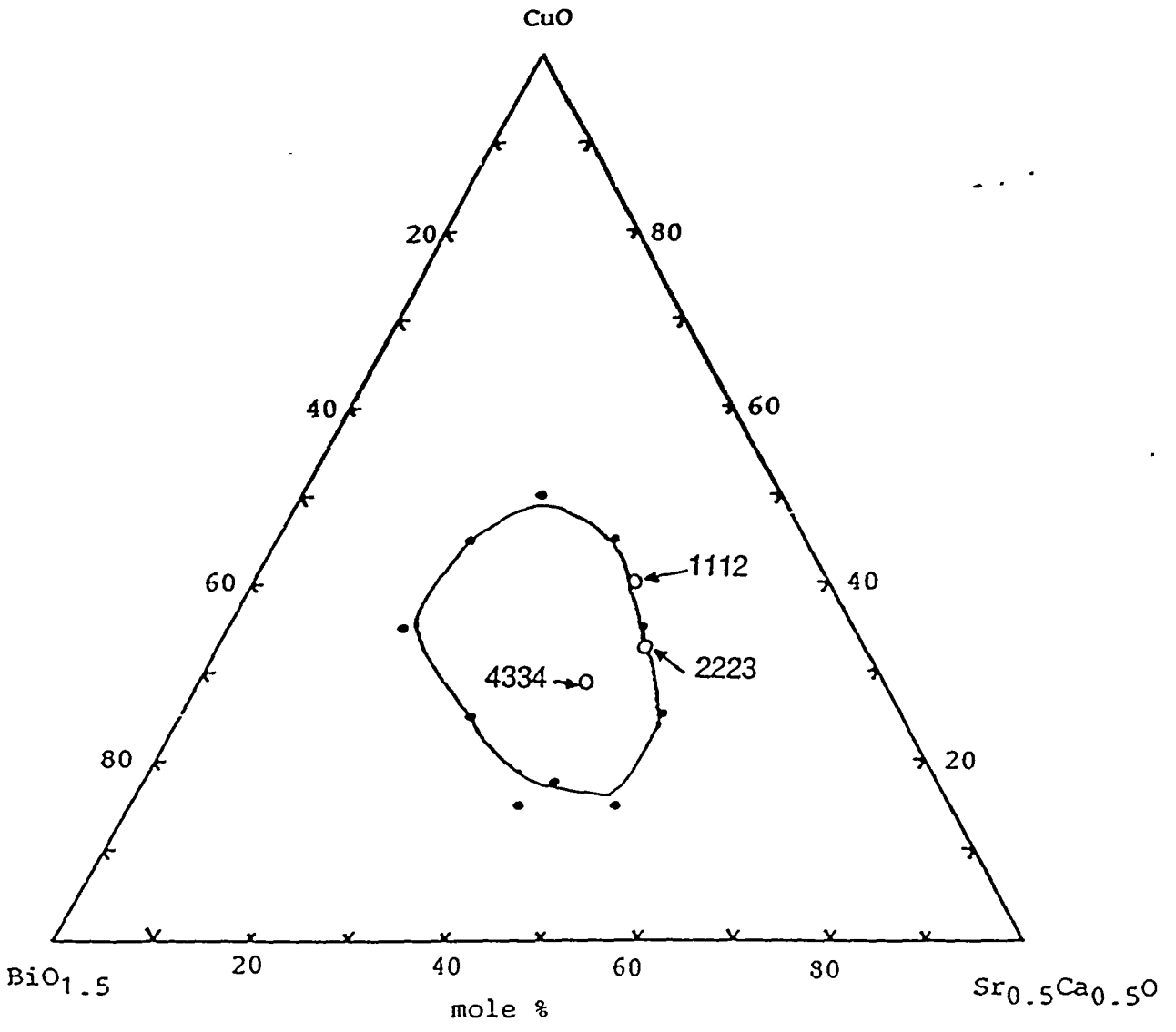


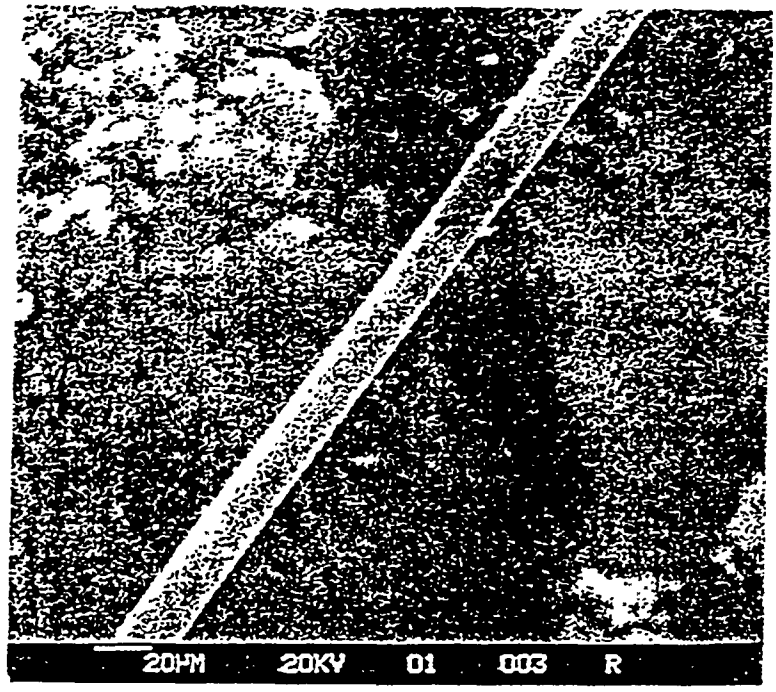
Figure 5. X-ray diffraction pattern of the thin film shows the C-axis matched orientations. (The thickness is about 1 mm.)

Figure 6. $Bi_4Ca_3Sr_3Cu_4O_{16}$ Superconducting Glass Ceramic Rod and Ring

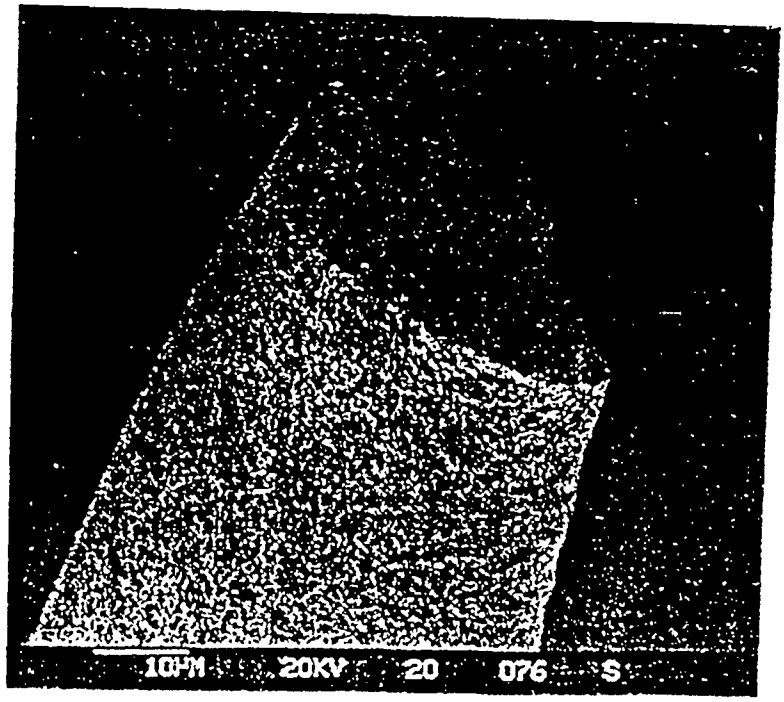


Glass Forming Range of $BiO_{1.5}$ -CuO-$Ca_{0.5}Sr_{0.5}O$ System

Figure 7.



Bi(Pb)-Ca-Sr-Cu-O glass fiber



Bi(Pb)-Ca-Sr-Cu-O ceramic fiber
from crystallization of glasses

Figure 8.

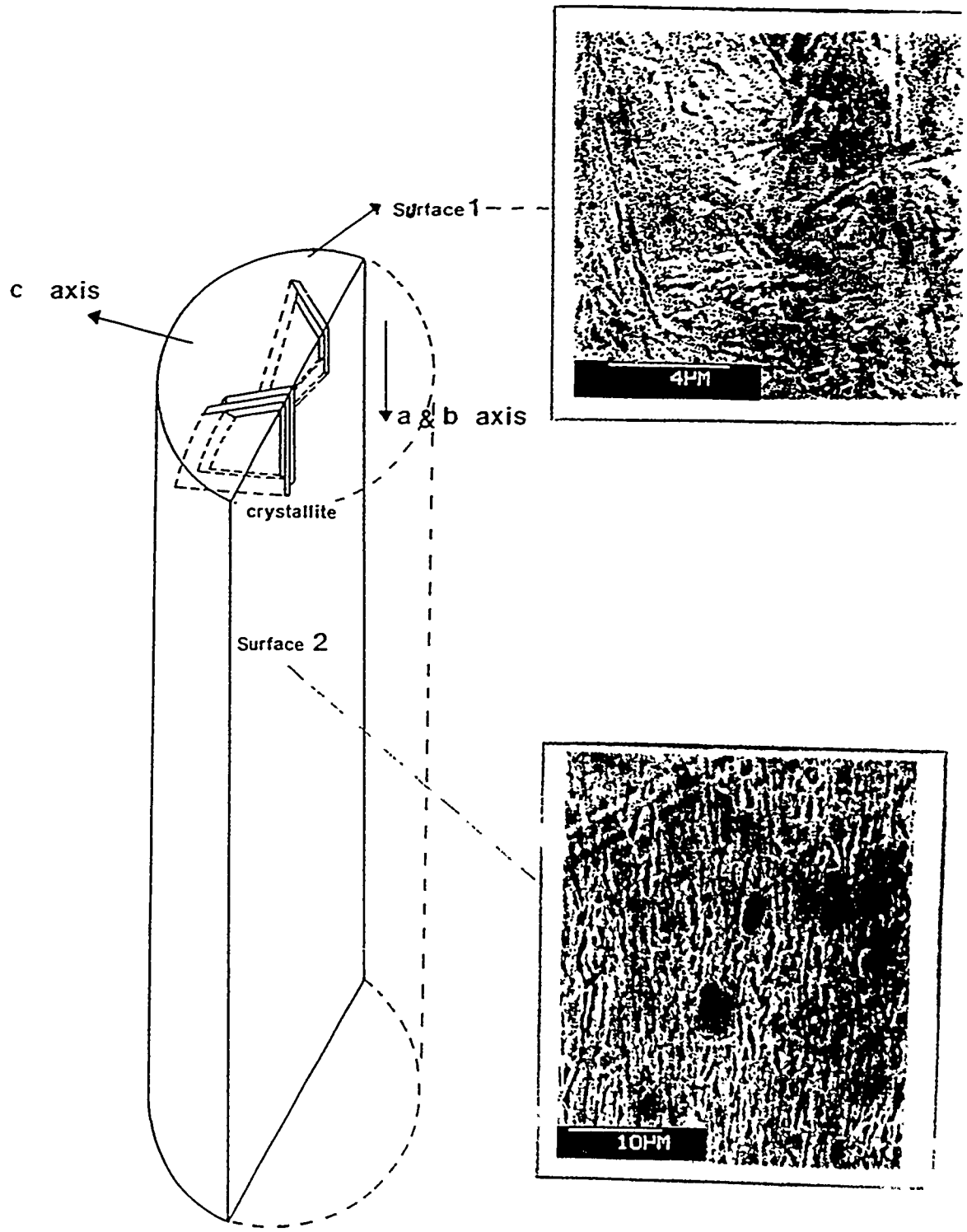


Figure 9. Glass Ceramic Rod Section

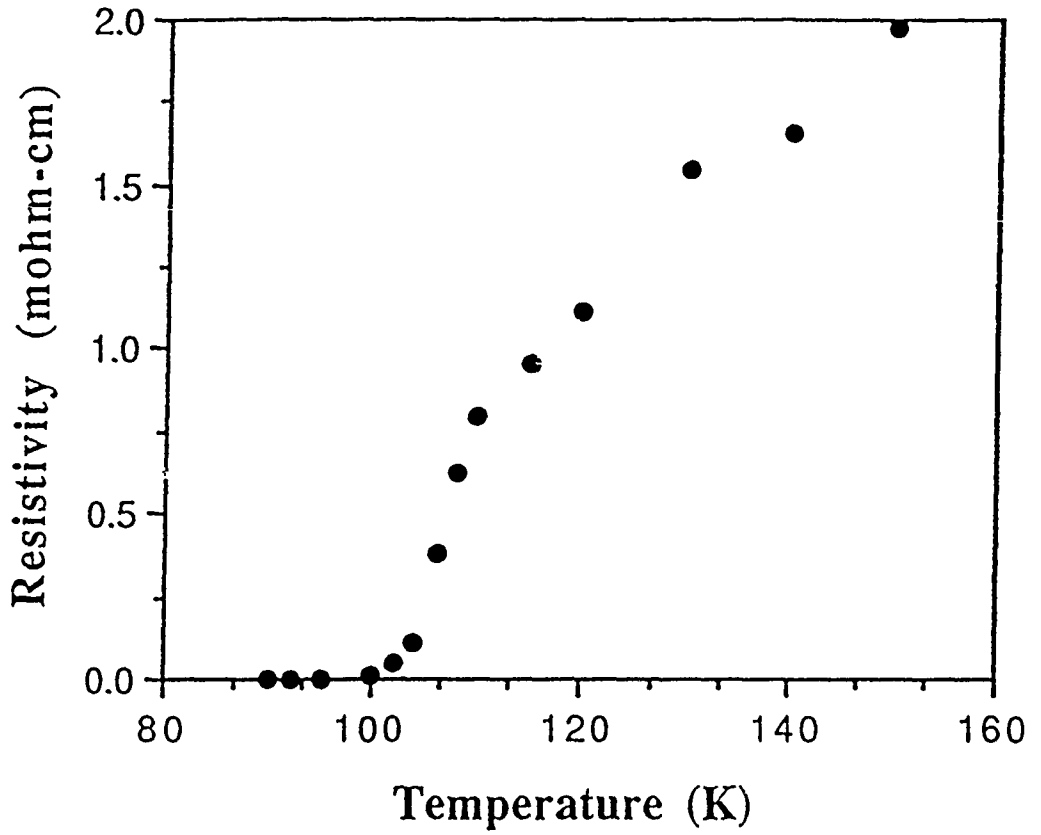


Figure 10. Dependence of electrical resistivity of the glass-ceramics: $Bi_{1.84}Pb_{0.34}Ca_2Sr_2Cu_4O_y$ (heat treated at 842°C for 120 hours in the atmosphere of Ar + O_2) on temperature.

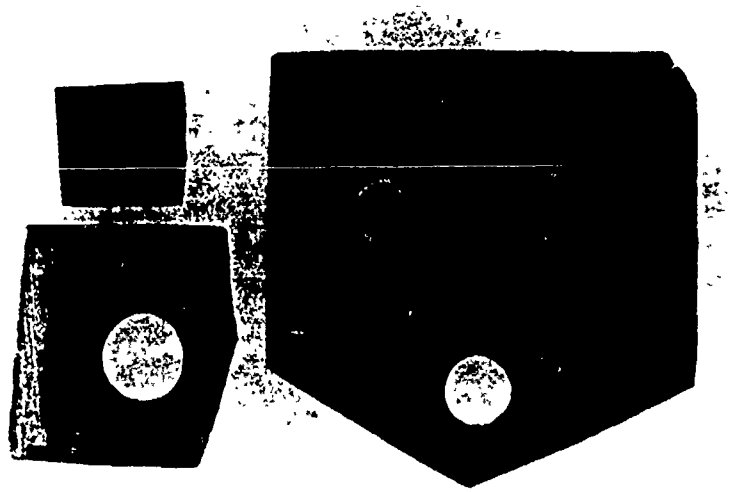
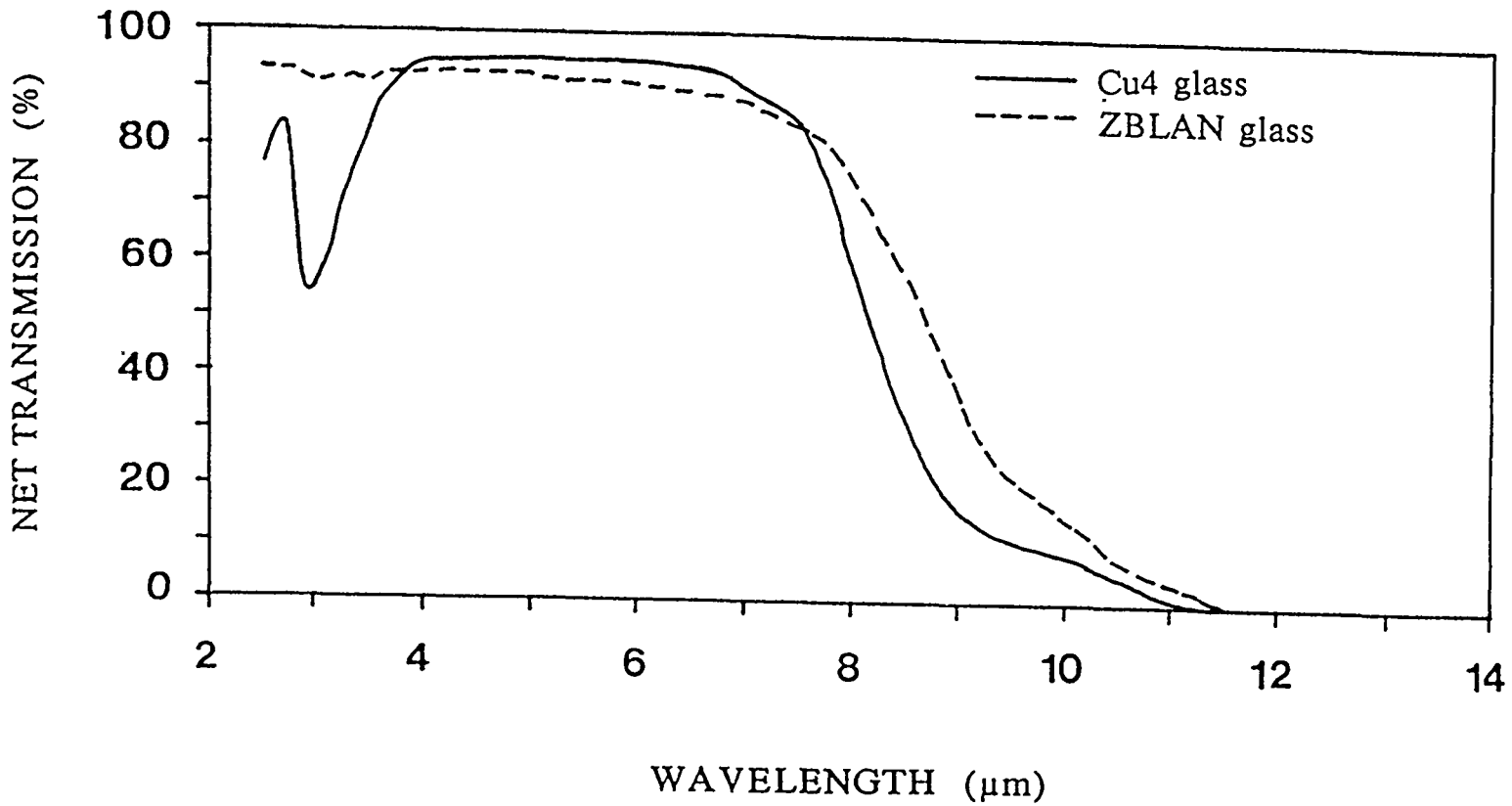


Figure 11. Machinable glass-ceramic superconductor based on the bismuth composition.



The net infrared transmission of Cu4 glass and 53ZrF4-20BaF2-4LaF3-3ALF3-20NaF glass

Figure 12

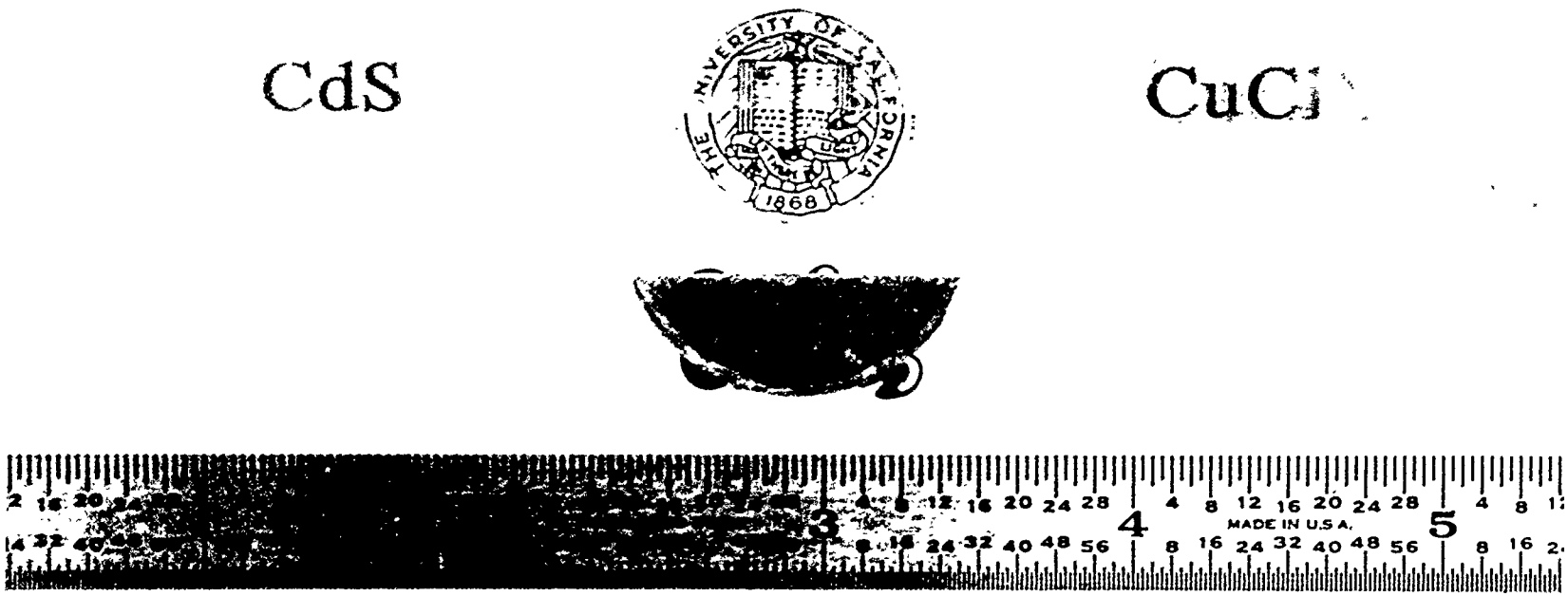
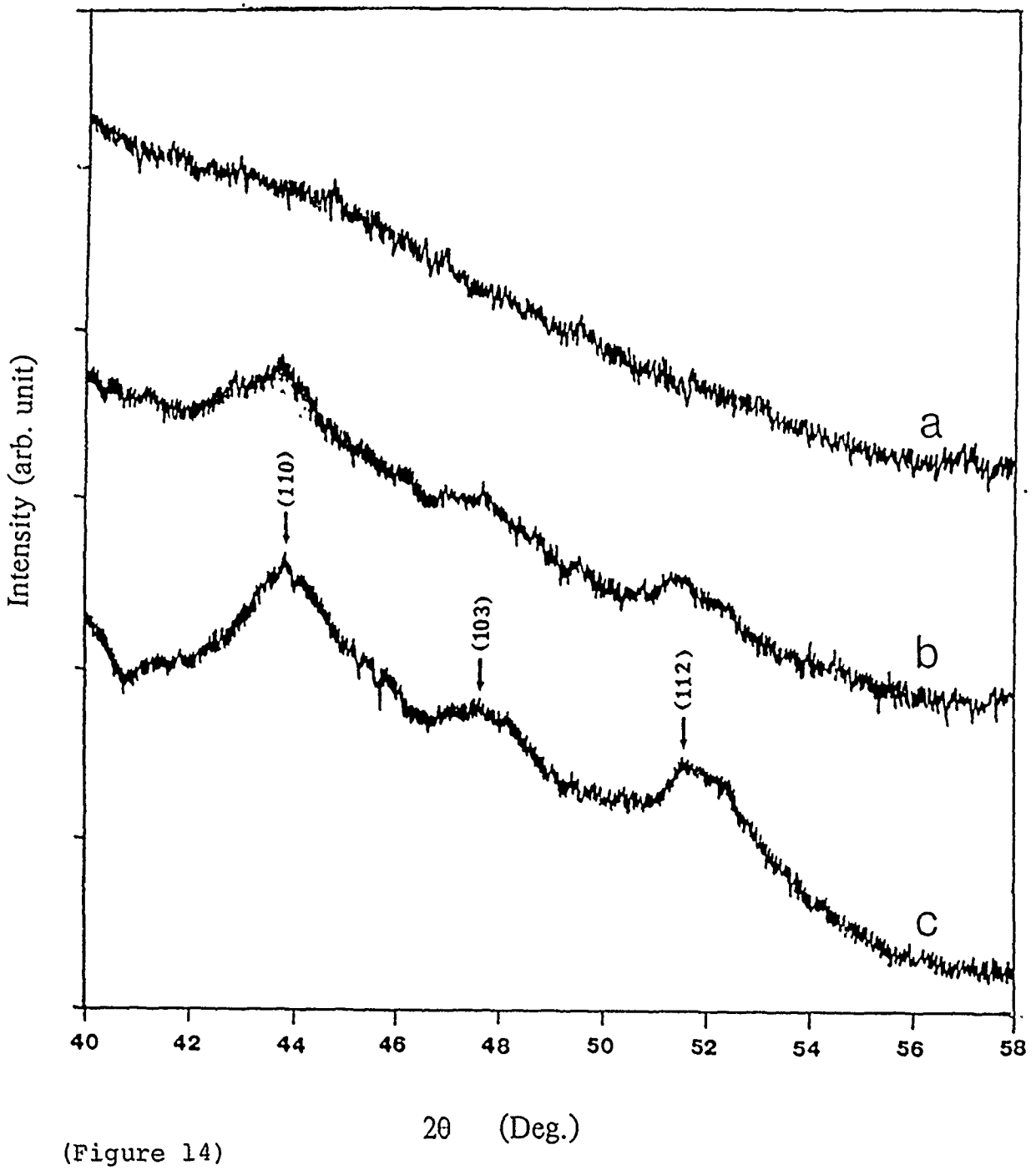


Figure 13 Transparent semiconductor-doped ormosils prepared by the sol-gel process.

X-Ray Diffraction Patterns of CdS-doped Ormosils



(Figure 14)

X-ray diffraction patterns of ormosils heated for 24 h at 380 °C (a), reacted with H_2S gas for 8 h at room temperature (b) and 72 h (c). The numbers in (c) are the indices of hexagonal CdS crystal.

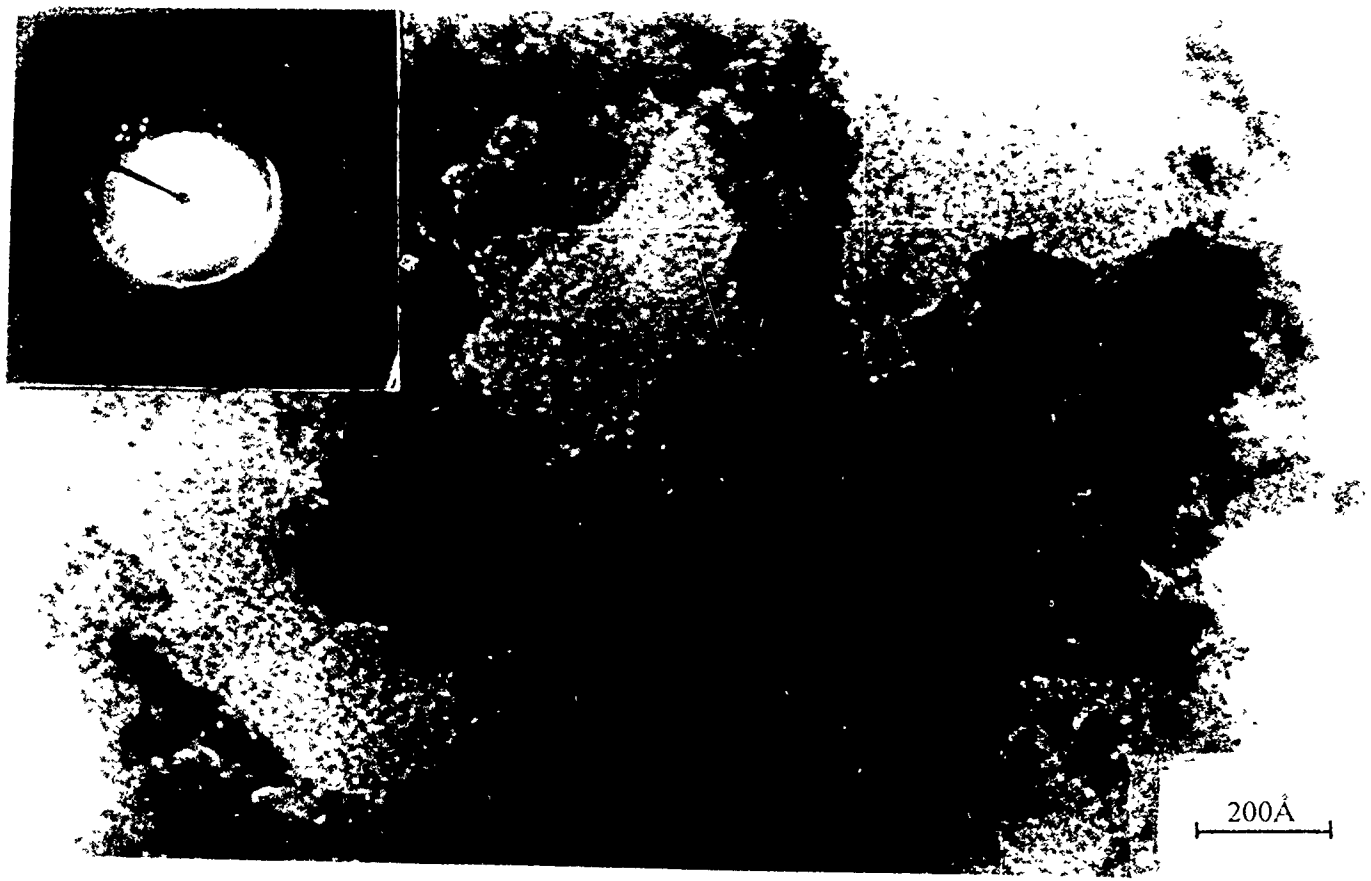
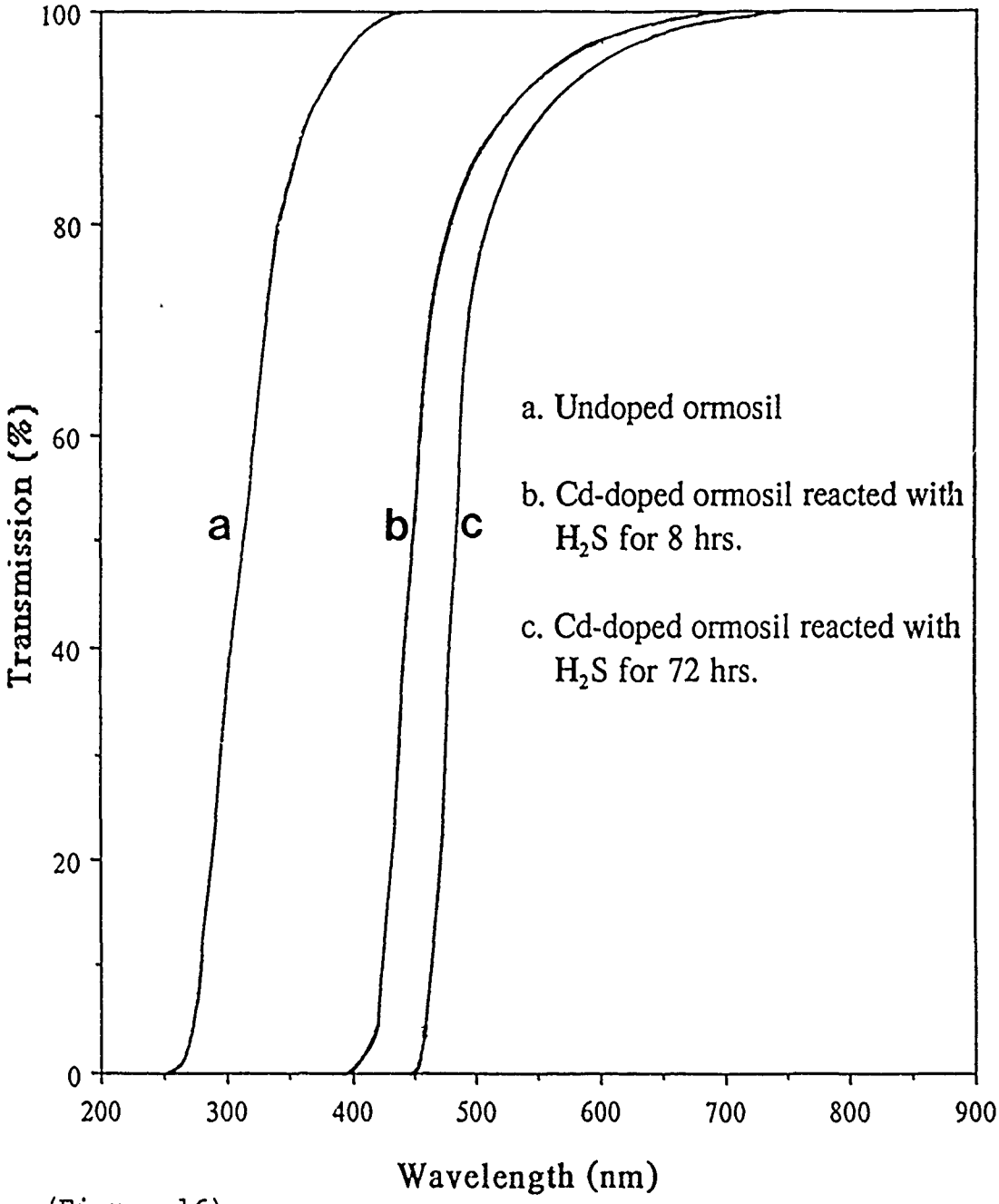


Figure 15 Transmission electron micrograph and (inset) electron diffraction pattern of ormosils reacted with H_2S for 72 h. CdS crystallites are seen as dark spheres with average size of 60Å. The electron diffraction pattern shows that CdS crystals have a hexagonal wurtzite structure.

Optical Transmission of CdS-doped Ormosil



(Figure 16)

The blue shift of curve b compared to c is a consequence of the quantum confinement effect due to smaller particle size.